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Simulation of an electrolytic bath for electrodeposition of multilayer shielding coatings

In this the calculation work galvanic bath of Cu/(Ni+Cu) multilayer shielding coatings formation from an acetate electrolyte containing 0,03 mol/L of $CuAc_2$, 0,3 mol/L of $NiAc_2$ and 1,66 mol/L of acetic acid were made. According to the results of polarization studies values of coatings deposition pulse mode current density have been chosen and current efficiency of copper and nickel during deposition of Cu-Ni alloy has been determined. To ensure a constant formulation of the electrolyte it has been proposed to use insoluble anodes made of stainless steel and continuous circulation of the electrolyte. The scheme of steams enabling the adjustment of the solution formulation with the use of an additional collecting vessel has been developed. The formulation of the correcting stream continuously fed into the collecting vessel has been calculated.

Key words: electrochemistry; simulation; cuprum acetate; nickel acetate; multilayer shielding coatings.

Introduction

Currently, there is an acute problem of protection devices and the environment from the effects of electromagnetic radiation. To ensure effective protection of the surface of plastics from which basic parts of devices are generally made, it is necessary to apply shielding coating. Multilayer coatings consisting of alternating layers of magnetic (e.g., nickel) and nonmagnetic (e.g., copper) metals are the most effective screens.

As shown by previous studies [1], copper filled composites consisting of an organic polymeric binder and a filler of copper powder can be used to create a conductive basis for a plastic for subsequent deposition of metal coatings. Shielding coatings consisting of alternating layers of copper and nickel, can be obtained by the «single-bath» method [2] from the electrolyte containing cations of the two metals Cu^{2+} and Ni^{2+}. Conditions for preparing of individual layers are provided with a pulsed electrolysis, in which an alternation of pulses with different values of current takes place. During odd pulses ions of the most electropositive nonmagnetic metal (copper) are recovering

$$Cu^{2+}+2\bar{e}\rightarrow Cu^0,$$

and during the even pulses ions of copper and nickel presented in the electrolyte are discharging to give a magnetic layer, and hydrogen gas is exhaling.

$$Cu^{2+}+2\bar{e}\rightarrow Cu^0$$

$$Ni^{2+}+2\bar{e}\rightarrow Ni^0$$

$$2H^{+}+2\bar{e}\rightarrow H_2$$

The purpose of the present work consisted in simulation of a galvanic bath for forming multilayer shielding coatings.

For electrodeposition layered Cu/(Ni+Cu) coating acetate electrolyte of the following composition: 0.03 mol/L of $CuAc_2$, 0,3 mol/L of $NiAc_2$ and 1.66 mol/L of acetic acid [2] has been used. Monitoring of value pH = 4.7 has been periodically conducted.

Experimental part

To select the parameters of the galvanic bath to be designed experimental studies were conducted.

Polarization measurements were carried out using a ZIVE SP5 electrochemical station with a linear change in the potential in the cell, connected by a three-electrode circuit.

The potential has been measured with respect to a silver chloride reference electrode.

When dotting the cathodic polarization curve (Fig. 1) the pin type working electrode made of copper wire with a diameter of 2 mm and a height of 10 mm has been used. The area on the curve corresponds to the limiting diffusion current of discharge of copper ions, and the subsequent rise of the current corresponds to recovery processes of nickel ions and hydrogen. According to the results of polarization studies current densities: for deposition of copper layer equals to 7 A/m^2 and a magnetic alloy Ni-Cu equals to 90 A/m^2 were selected.

The use of soluble anodes will lead to the enrichment of the electrolyte by nickel or copper ions, so it was proposed to use insoluble anodes made of stainless steel 12X18H10T. During polarization studies it was found that anodes made of steel are passivated and not dissolved in the solution.

For technological calculations current efficiency of metal has a great significance. During odd pulses copper recovery with 100 % current efficiency occurs.

To determine the current efficiency of metals during deposition of the magnetic layer experiments on deposition of a Ni-Cu coating to sample of stainless steel pre-coated by a copper layer were conducted. At a current density of 90 A/m^2 current efficiency of Ni-Cu alloy was 70.6 %.

The resulting precipitate of alloy and the copper underlayer have been dissolved in concentrated nitric acid. The concentration of Ni^{2+} ions in the resulting solution has been determined by photometry allowing estimating the mass of nickel in the alloy. The analysis was

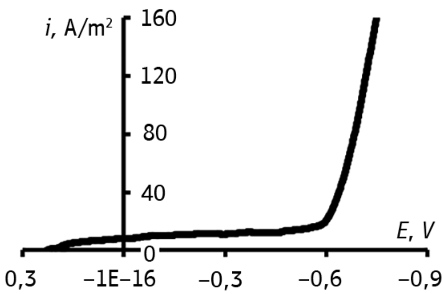

Fig. 1. Cathode polarization curve of the recovery of copper in acetate electrolyte

conducted by employees of the Department of Analytical Chemistry, CTI, UrFU. From the known weight of the precipitate alloy formulation was calculated as comprising 60 wt. % of Ni and 40 wt. % of Cu. The current efficiency of metals has been calculated taking into account proportion of the appropriate metal in the alloy

$$Bm_{\mathrm{Ni}} = Bm_{alloy} \cdot \omega_{\mathrm{Ni}} = 70 \cdot 0{,}6 = 42\ \%,$$
$$Bm_{\mathrm{Cu}} = Bm_{alloy} \cdot \omega_{\mathrm{Cu}} = 70 \cdot 0{,}4 = 28\ \%.$$

The summarized reaction occurring during the even pulses based on the current efficiency looks as follows:

$$\text{Вт}_{cu}\cdot \mathrm{CuAc_2} + \text{Вт}_{\mathrm{Ni}}\cdot \mathrm{NiAc_2} + \mathrm{H_2O} =$$
$$\text{Вт}_{cu}\cdot \mathrm{Cu} + \text{Вт}_{\mathrm{Ni}}\cdot \mathrm{Ni} + (1\text{-Вт}_{\mathrm{Cu}}\text{-Вт}_{\mathrm{Ni}})\cdot \mathrm{H_2}\uparrow +$$
$$+(2-1+\text{Вт}_{\mathrm{Cu}}+\text{Вт}_{\mathrm{Ni}})\cdot \mathrm{HAc}$$

From the latter equation it follows that when using insoluble anodes in the electrolysis process a reduction in the concentration of copper and nickel acetates in a solution will be observed, and the concentration of acetic acid will increase.

Discussion of the calculations results

For the stable operation of the galvanic bath and preparing precipitates of high quality it is necessary to maintain the formulation of the electrolyte unchanged. In the projected bath it can be achieved by adjusting the formulation of continuous circulating flow at the inlet to the bath.

A scheme has been proposed (Fig. 2), which includes a collecting vessel intended for the organization of continuous circulation of the solution and adjusting its formulation. Electrolyte discharged from the bath is divided into two streams, one is directed to the collecting vessel ($½\vartheta_1$), and the second one is directed to neutralize acid excess ($½\vartheta_1$). Simultaneously, correcting stream (ϑ_{cor}) is fed to the collecting vessel, wherein the concentration of copper and nickel acetates is higher than in the bath. The effluent solution from the collecting vessel is fed into a galvanic bath (ϑ'_1). Furthermore, during the process calculations speed of pseudocontinuous streams (ϑ'_1 and ϑ_2), which are solutions transferred on details, was considerd.

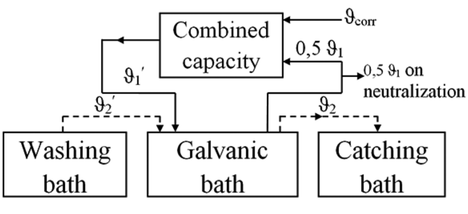

Fig. 2. Correcting streams in the technological scheme of multilayer coating deposition

As the result of the calculation of the stationary mass balance of the galvanic bath it was found that for stable operation it is necessary that the electrolyte is fed to the bath, wherein the acetic acid concentration (C'_{HAc} = 1,48 mol/L) is below, and the concentrations of copper acetate (C'_{HAc2} = 0,033 mol/L) and nickel acetate (C'_{HAc2} = 0,304 mol/L) is higher than in the bath. In view of water evaporation rate defined was a volume rate of effluent stream from which then stream feeding to the collecting vessel is formed. While calculating the different values of intensities of components sources in periods of even and odd pulses were taken into account.

The correcting stream is needed to maintain in the collecting vessel a constant formulation of the solution corresponding by components concentrations to a stream directed to the bath of multilayer coating deposition.

Simulation of the stationary mass balance of the collecting vessel has allowed determining the rate of the correcting stream and its formulation:

$$\vartheta_{cor} = \vartheta_1^{'} - \frac{\vartheta_2}{2},$$

$$C_{cor,i} = \frac{\vartheta_1^{'} \cdot C_{1i}^{'} - \vartheta_1 / 2 \cdot C_{1i}}{\vartheta_{cor}}.$$

The calculation has showed that the solution containing 1.45 mol/L of acetic acid, 0.037 mol/L of copper acetate and 0.307 mol/L of nickel acetate should be continuously added at a rate equal to $\vartheta_{cor} = 5{,}0 \cdot 10^{-6}$ m^3/s to the collecting vessel.

Conclusion

During the experimental studies the parameters of pulse mode of multilayer coating deposition, and current efficiency of copper and nickel have been determined.

For preparing layered Cu/Cu-Ni coatings by the single-bath method it has been proposed to use a continuous flow bath with insoluble anodes. The possibility of using stainless steel as an insoluble anode in an acetate electrolyte has been shown.

Using the method of mathematical modeling of mass balances of galvanic baths and the collecting vessel the formulation of the circulating stream incoming to the bath as well as the speed and formulation of the correcting stream incoming to the collecting vessel have been determined.

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